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[JP,2003-313435,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

JP,2003-313435,1. A

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]This invention is excellent in dynamic physical properties, dimensional stability, heat resistance, etc., and relates to the charge of insulating-substrate material which has the outstanding fire retardancy especially by the shape retention effect at the time of combustion, a laminate sheet, a printed circuit board, copper foil with resin, copper clad laminate, a polyimide film, the film for TAB, and prepreg.

[0001]

[Description of the Prior Art]Generally, the multilayer printed board used for electronic equipment is constituted by the insulating substrate of two or more layers.

Although manufactured by the build up method for obtaining multilayered laminate by repeating the circuit formation on a layer, and lamination, the package laminated layers method which laminates collectively the layer in which the circuit was formed, etc., Also in which manufacturing method, since there are many routing counters, and the quality of material influences the yield greatly and includes processes, such as a plating process, a curing process, and a solder reflow process, solvent resistance, a water resisting property, the dimensional

stability in heat resistance and an elevated temperature, etc. are required of material. Specifically, for example Acid, Tolerance to alkali and an organic solvent; To an electrical property, influence. dimensional stability [after the time of the elevated temperature which affects the highly precise circuit connection between thing; up-and-down layers with little moisture absorption to give, and heating]; -- heat-resistant [up to 260 ** required for mounting with lead free solder]; -- it is required that the migration of the copper which affects connection reliability should not happen easily etc.

[0002]Conventionally, as an insulating substrate, the thermosetting resin prepreg which impregnated glass fabrics with thermosetting resin, and the film which consists of thermosetting resin or a photo-setting resin have been used, for example. In recent years, to make between layers very thin also in a multilayer printed board for densification and slimming down is desired, and the layer insulation board which does not use the thin layer insulation board using glass fabrics or glass fabrics is needed.

[0003]As such an insulating substrate, what consists of a charge of a thermosetting resin material which denaturalized with rubbers (elastomer), an acrylic resin, etc., thermoplastics material which blended the inorganic bulking agent in large quantities, etc. is known, for example. For example, the inorganic bulking agent which has predetermined particle diameter is blended with the varnish which uses the amount epoxy polymer of polymers, a polyfunctional epoxy resin, etc. as the main ingredients, and the manufacturing method of the multilayer insulating substrate which is applied to a base material and made into an insulating layer is indicated by the patent documents 1. In this insulating substrate, the improvement of a high temperature physical property is also achieved by using together the epoxy resin which has the outstanding heat resistance, and an inorganic bulking agent.

[0004]However, in the multilayer insulating substrate produced by the above-mentioned manufacturing method. In order to secure the interfacial area of an inorganic bulking agent, and the amount epoxy polymer of polymers and a polyfunctional epoxy resin and to fully raise dynamic physical properties, such as a mechanical strength, A lot of inorganic bulking agents needed to be blended, and there was a problem that the fault on processing of the increase in a manufacturing process, etc. arose, or it was difficult to make between layers thin. In the temperature more than glass transition temperature, most improvement effects of physical properties are not seen, and at the temperature below glass transition temperature, their improvement effect is small and cannot expect them about the improvement effect of hygroscopicity or solvent resistance, either.

[0005]In order to raise the dynamic physical properties of resin as the patent documents 2 are also indicated, adding an inorganic compound to resin generally is performed.

For example, in order to raise the rigidity of resin, talc, calcium carbonate, etc. are added by resin. It is thought that dynamic physical properties improve by adding an inorganic compound to resin because a pitch child is restrained on the surface of an inorganic compound, and in order to fully raise the dynamic physical properties of resin, it is necessary to take the large interface product of an inorganic compound and a pitch child.

[0006]Common inorganic compounds are tens - a size of 100 micrometers of numbers, and in order to acquire sufficient dynamic physical-properties improved effect, they usually need to be added 100 or more weight sections to resin 100 weight section. However, when an inorganic compound is added in large quantities, there is a problem that will be in the state of what is called a trade-off where the original toughness of resin and shock resistance fall, lightweight nature is lost, or a moldability falls.

[0007]Thus, the problem that heat resistance, dimensional stability, etc. are insufficient, and since it was easy to be divided easily, problems -- fault arises in a manufacturing process in many cases etc. -- were among the layer insulation boards which do not use the thin layer insulation board using glass fabrics or glass fabrics.

[0008]The sheet silicate attracts attention by a little addition in recent years as an inorganic compound in which a big interface product with resin is obtained, and a very big interface product is obtained by carrying out exfoliation distribution of this into resin. In the nonpatent literature 1, it is reported by thermoplastics that pulled by having added the sheet silicate 4.2% of the weight, and having carried out exfoliation distribution into nylon, and the elastic modulus improved 1.9 times.

[0009]After mixing the organicity-sized sheet silicate and the epoxy resin of a bisphenol A type at 80 ** in the patent documents 3 with thermosetting resin, The method of carrying out exfoliation distribution of the sheet silicate into an epoxy resin by carrying out compression molding of the mixture obtained by mixing with the amino diphenylsulfone of a hardening agent at 200 ** is indicated. However, with a described method, a complicated process is needed and also there was a problem that it was difficult to manufacture a thin Plastic solid etc., with compression molding.

[0010]On the other hand, the polymer material used for an industrial use way is expected the conversion to environment-friendly environmental adaptation die materials from the problem of processing of waste, environmental hormone, etc. in recent years. The conversion to non halogen type fire retardant from halogen-containing mold fire retardant is considered, and, specifically, the so-called establishment of the flameproofing treatment technique which does not use halogen-containing mold fire retardant, and non halogen flameproofing treatment technique is desired strongly, for example. Although it has the advantage that the above-mentioned halogen-containing mold fire retardant has a high effect of flameproofing, and there are comparatively few falls of a moldability, falls of the dynamic physical properties of mold goods, etc., There is a possibility of generating halogen system gas, such as a lot of dioxin at the time of a fabricating operation and combustion, and the emitted halogen system gas makes apparatus corrode, or has an adverse effect on a human body.

[0011]For this reason, also in charges of insulating-substrate material, such as a resin sheet, development of the material which uses non halogen type fire retardant for conversion to environmental adaptation die materials is made in recent years. However, in order to make required fire retardancy reveal, a lot of non halogen type fire retardant needed to be blended, and in heat resistance, dimensional stability, etc., there was a problem of being less than the conventional charge of insulating-substrate material which uses halogen-containing mold fire

retardant.

[0012]When the charge of insulating-substrate material is made into a thin shape, thus, heat resistance, dimensional stability, And dynamic physical properties fell, and in order to make sufficient fire retardancy reveal, without using halogen-containing mold fire retardant, when a lot of non halogen type fire retardant was blended with the charge of insulating-substrate material, there was a problem that dynamic physical properties, heat resistance, etc. were not obtained.

[0013]

[Patent documents 1] JP,2000-183539,A[Patent documents 2] JP,2000-193539,A[Patent documents 3] The patent No. 3014674 gazette [Nonpatent literature 1] Polymers, 42 (the July item), 589 (1993)

[0014]

[Problem(s) to be Solved by the Invention]This invention is excellent in dynamic physical properties, dimensional stability, heat resistance, etc. in view of the above-mentioned actual condition, It aims at providing the charge of insulating-substrate material which has the outstanding fire retardancy especially by the shape retention effect at the time of combustion, a laminate sheet, a printed circuit board, copper foil with resin, copper clad laminate, a polyimide film, the film for TAB, and prepreg.

[0015]

[Means for Solving the Problem]Resin 100 weight section which this invention becomes from at least one sort of thermosetting resin, and/or thermoplastics, Are a charge of insulating-substrate material obtained by drying a resin varnish constituent containing 0.1 to sheet silicate 100 weight section, and 30 to organic solvent 1000 weight section, and said sheet silicate, Average interlaminar distance of a field measured by a wide angle X diffraction measuring method (001) is not less than 3 nm, and it is the charge of insulating-substrate material which all are distributing as a layered product of five or less layers in part. This invention is explained in full detail below.

[0016]A charge of insulating-substrate material of this invention is obtained by drying a resin varnish constituent containing resin which consists of at least one sort of thermosetting resin, and/or thermoplastics, 0.1 to sheet silicate 100 weight section, and 30 to organic solvent 1000 weight section.

[0017]at ordinary temperature, the above-mentioned thermosetting resin is a liquid, the shape of a semi solid, or a solid state, and shows mobility under ordinary temperature or heating -- a substance of low molecular weight comparatively, Resin of insoluble and infusible nature which forms the three-dimensional structure of mesh shape is meant causing chemical reactions, such as a hardening reaction and crosslinking reaction, and increasing a molecular weight by operation of a hardening agent, a catalyst, or heat.

[0018]It is not limited especially as the above-mentioned thermosetting resin, but For example, epoxy system resin, Heat-hardened type modified-polyphenylene-ether system resin, heat-hardened type polyimide system resin, Urea system resin, allylic resin, silicone resin, benzoxazine system resin, phenol system resin, unsaturation polyester system resin, bismaleimide triazine resin, alkyd system resin, furan system resin, melamine system resin, polyurethane

system resin, aniline system resin, etc. are mentioned. Especially, epoxy system resin, heat-hardened type modified-polyphenylene-ether system resin, heat-hardened type polyimide resin, urea system resin, allylic resin, silicone resin, benzoxazine system resin, phenol system resin, unsaturation polyester system resin, bismaleimide triazine resin, etc. are preferred. These thermosetting resin may be used independently and two or more sorts may be used together.

[0019]The above-mentioned epoxy resin refers to an organic compound which has at least one oxirane ring (epoxy group). As the number of epoxy groups in the above-mentioned epoxy resin, it is preferred that it is one or more per molecule, and it is more preferred that it is two or more per molecule. Here, the number of epoxy groups per molecule is called for by doing division of the total of an epoxy group in an epoxy resin in a total of a molecule in an epoxy resin.

[0020]An epoxy resin (1) - an epoxy resin (11), etc. which were not limited, could use a publicly known epoxy resin conventionally especially as the above-mentioned epoxy resin, for example, were shown below are mentioned. These epoxy resins may be used independently and two or more sorts may be used together.

[0021]As the above-mentioned epoxy resin (1), for example A bisphenol A type epoxy resin, Bisphenol F type epoxy resin, a bisphenol A D type epoxy resin, Bisphenol type epoxy resin, such as a bisphenol smooth S form epoxy resin; Phenol novolak type epoxy resin, Novolak type epoxy resin, such as cresol novolak type epoxy resin; aromatic epoxy resin, these hydrogenation ghosts, bromination things, etc., such as trisphenol methane triglycidyl ether, are mentioned.

[0022]As the above-mentioned epoxy resin (2), for example 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, A bis(3,4 - epoxycyclohexyl)horse mackerel peat, a bis(3, 4-epoxycyclohexylmethyl)horse mackerel peat, A bis(3,4-epoxy-6-methylcyclohexylmethyl)horse mackerel peat, Alicycle fellows epoxy resins, such as 2-(3,4-epoxycyclohexyl 5,5-spiro3,4-epoxy) cyclohexanone metha- dioxane and bis(2,3-epoxy cyclopentyl)ether, etc. are mentioned. As what is marketed among these epoxy resins (2), a trade name "EHPE-3150" (softening temperature of 71 **, Daicel Chemical Industries, Ltd. make) etc. are mentioned, for example.

[0023]As the above-mentioned epoxy resin (3), for example Diglycidyl ether of 1,4-butanediol, Diglycidyl ether of 1,6-hexanediol, triglycidyl ether of glycerin, Triglycidyl ether of trimethylolpropane, diglycidyl ether of a polyethylene glycol, Diglycidyl ether of a polypropylene glycol, Aliphatic series epoxy resins etc. in which a carbon number contains polyoxy alkylene glycol containing an alkylene group of 2-9 (preferably 2-4), polytetramethylene ether glycol, etc., such as poly glycidyl ether of long chain polyol, are mentioned.

[0024]As the above-mentioned epoxy resin (4), for example Phthalic acid diglycidyl ester, Tetrahydrophthal acid diglycidyl ester, diglycidyl hexahydrophthalate, Glycidyl ester typed epoxy resin, these hydrogenation ghosts, etc., such as glycidyl ether glycidyl ester of diglycidyl p-oxybenzoic acid and salicylic acid and dimer acid glycidyl ester, are mentioned.

[0025]As the above-mentioned epoxy resin (5), for example Triglycidyl isocyanurate, Glycidyl amine type epoxy resin, these hydrogenation ghosts, etc., such as N [of a N,N'-diglycidyl derivative of annular alkylene urea, a N,N,O-triglycidyl derivative of p-aminophenol, and m-

aminophenol], N, and O-triglycidyl derivative, are mentioned.

[0026]As the above-mentioned epoxy resin (6), a copolymer of glycidyl (meta) acrylate and radical polymerization nature monomers, such as ethylene, vinyl acetate, and acrylic ester (meta), etc. are mentioned, for example. In this specification, an acrylic (meta) means an acrylic or methacrylic one.

[0027]What epoxidated a double bond of unsaturated carbon in a polymer which makes conjugated diene compounds, such as epoxidation polybutadiene, a subject, or a polymer of the partially-hydrogenated thing as the above-mentioned epoxy resin (7), for example is mentioned.

[0028]A polymeric block which makes vinyl aromatic compounds, such as epoxidation SBS, a subject as the above-mentioned epoxy resin (8), for example, What epoxidated a double bond of unsaturated carbon of a conjugated diene compound in a block copolymer which has a polymeric block which makes a conjugated diene compound a subject, or a polymeric block of the partially-hydrogenated thing in the same intramolecular is mentioned.

[0029]As the above-mentioned epoxy resin (9), one or more polyester resin per molecule etc. which have two or more epoxy groups preferably are mentioned, for example.

[0030]As the above-mentioned epoxy resin (10), a urethane conversion epoxy resin, a polycaprolactone conversion epoxy resin, etc. which introduced a urethane bond and polycaprolactone combination into structure of above-mentioned epoxy resin (1) - (9) are mentioned, for example.

[0031]As the above-mentioned epoxy resin (11), a rubber conversion epoxy resin etc. which made above-mentioned epoxy resin (1) - (10) contain rubber compositions, such as NBR, CTBN, polybutadiene, and acrylic rubber, are mentioned, for example.

[0032]It is not limited especially as a hardening agent used for a hardening reaction of the above-mentioned epoxy resin. Can use a publicly known hardening agent for epoxy resins conventionally, and For example, an amine compound, Compounds, such as a polyamino amide compound compounded from an amine compound, a tertiary amine compound, An imidazole compound, a hydrazide compound, a melamine compound, an acid anhydride, a phenolic compound, a heat latency cationic polymerization catalyst, an optical latency cationic initiator, cyanogen amide, its derivative, etc. are mentioned. These hardening agents may be used independently and two or more sorts may be used together.

[0033]It is not limited especially as the above-mentioned amine compound, but For example, ethylenediamine, Diethylenetriamine, triethylenetetramine, tetraethylenepentamine, Chain fatty amine and its derivatives, such as polyoxy propylenediamine and polyoxypropylene triamine; MENSENJI amine, Isophorone diamine, bis(4-amino-3-methylcyclohexyl)methane, Diaminohexylmethane, bis(aminomethyl)cyclohexane, Annular fatty amine and its derivatives, such as N-aminoethyl piperazine and a 3,9-bis(3-aminopropyl)2,4,8,10-tetraoxaspiro (5, 5) undecane; M-xylenediamine, Aromatic amines, such as alpha-(m/p aminophenyl) ethylamine, m-phenylenediamine, diaminodiphenylmethane, diaminodiphenyl sulfone, alpha, and alpha-bis(4-aminophenyl)-p-diisopropylbenzene, a derivative of those, etc. are mentioned.

[0034]It is not limited especially as a compound compounded from the above-mentioned amine

compound, but For example, the above-mentioned amine compound, Succinic acid, adipic acid, azelaic acid, sebacic acid, dodeca diacid, isophthalic acid, A polyamino amide compound compounded from carboxylic acid compounds, such as terephthalic acid, dihydroisophthalic acid, tetrahydro isophthalic acid, and hexahydro isophthalic acid, and its derivative; The above-mentioned amine compound, A ketimine compound compounded from a polyamino imide compound compounded from maleimide compounds, such as diaminodiphenylmethane bismaleimide, and its derivative; above-mentioned amine compound and ketone compound, and its derivative; The above-mentioned amine compound, an epoxy compound, urea, thiourea, A poly amino compound compounded from compounds, such as an aldehyde compound, a phenolic compound, and an acrylic compound, its derivative, etc. are mentioned.

[0035]It is not limited especially as the above-mentioned tertiary amine compound, but For example, a N,N-dimethylpiperazine, Pyridine, picoline, benzyldimethylamine, 2-(dimethyl aminomethyl) phenol, 2,4,6-tris(dimethyl aminomethyl) phenol, the 1,8-diaza screw cyclo (5, 4, 0) undecene 1, its derivative, etc. are mentioned.

[0036]It is not limited especially as the above-mentioned imidazole compound, for example, 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, its derivative, etc. are mentioned.

[0037]It is not limited especially as the above-mentioned hydrazide compound, but For example, 1,3-bis(hydrazinocarboethyl)-5-isopropylhydantoin, 7,11-octadecadiene- 1,18-dicarbohydrazide, eicosane diacid dihydrazide, adipic acid dihydrazide, its derivative, etc. are mentioned.

[0038]It is not limited especially as the above-mentioned melamine compound, for example, 2,4-diamino-6-vinyl-1,3,5-triazine, its derivative, etc. are mentioned.

[0039]It is not limited especially as the above-mentioned acid anhydride, but For example, a phthalic acid anhydride, trimellitic anhydride, A pyromellitic anhydride, a benzophenone tetracarboxylic anhydride, ethylene glycol screw anhydrotrimellitate, Glycerol tris anhydrotrimellitate, methyl cyclohexene-dicarboxylic anhydride, Tetrahydro phthalic anhydride, a NAJIKKU acid anhydride, a methyl NAJIKKU acid anhydride, Trialkyl tetrahydro phthalic anhydride, hexahydro phthalic anhydride, Methylhexahydrophthalic anhydride, the 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene 1, 2-dicarboxylic anhydride, A trialkyl tetrahydro phthalic anhydride-maleic anhydride addition, a dodecenyl succinic anhydride, a poly azelain acid anhydride, a polydodecanedioic anhydride, a chlorendic anhydride, its derivative, etc. are mentioned.

[0040]It is not limited especially as the above-mentioned phenolic compound, for example, phenol novolac, o-cresolnovolak, p-cresolnovolak, t-butylphenol novolac, dicyclopentadiene cresol, its derivative, etc. are mentioned.

[0041]It is not limited especially as the above-mentioned heat latency cationic polymerization catalyst, but For example, 6 antimony fluoride, Benzylsulfonium salt which used 6 phosphorus fluorides, 4 boron fluoride, etc. as an opposite anion, Nonionic heat latency cationic polymerization catalysts, such as ionicity heat latency cationic polymerization catalyst;N-benzylphthalimides, such as a benzylammonium salt, benzylpyridinium salt, and benzyl

phosphonium salt, and aromatic-sulfonic-acid ester, are mentioned.

[0042]It is not limited especially as the above-mentioned optical latency cationic initiator. . For example, used 6 antimony fluoride, 6 phosphorus fluorides, 4 boron fluoride, etc. as an opposite anion. Onium salt, such as aromatic diazonium salt, an aromatic halo NIUMU salt, and aromatic sulfonium salt. And ionicity light latency cationic initiators, such as organometallic complexes, such as an iron-allene complex, a titanocene complex, and an aryl silanol aluminium complex; Nitrobenzyl ester, Nonionic light latency cationic initiators, such as a sulfonic acid derivative, phosphoric ester, phenolsulfonic acid ester, an diazonaphthoquinone, and N-hydroxy imide SUHONATO, are mentioned.

[0043]It is not limited especially as the above-mentioned heat-hardened type modified-polyphenylene-ether system resin, for example, resin etc. which denaturalized by a functional group which has thermosetting, such as a glycidyl group, an isocyanate group, and an amino group, are mentioned in the above-mentioned polyphenylene ether system resin. These heat-hardened type modified-polyphenylene-ether system resin may be used independently, and two or more sorts may be used together.

[0044]Especially if it is resin which has imide bonding in a molecule main chain as the above-mentioned thermosetting polyimide system resin, will not be limited, but specifically, For example, a condensation polymer of aromatic diamine and aromatic tetracarboxylic acid, A bismaleimide resin which is an addition polymer of aromatic diamine and bismaleimide, Bismaleimide triazine resin etc. which consist of a polyamino bismaleimide resin which is an addition polymer of aminobenzoic acid hydrazide and bismaleimide, and a JISHIANETO compound and a bismaleimide resin are mentioned. Especially, bismaleimide triazine resin is used suitably. These thermosetting polyimide system resin may be used independently, and two or more sorts may be used together.

[0045]It will not be limited especially if it is thermosetting resin obtained at an addition condensation reaction of urea and formaldehyde as the above-mentioned urea resin. It is not limited especially as a hardening agent used for a hardening reaction of the above-mentioned urea resin, For example, inorganic acid, organic acid, an actual nature hardening agent that consists of acid salt like acid sodium sulfate; a latent curing agent like salts, such as carboxylate, an acid anhydride, ammonium chloride, and ammonium phosphate, is mentioned. Especially, storage life etc. to a latent curing agent is preferred.

[0046]As the above-mentioned allylic resin, especially if obtained by a polymerization and a hardening reaction of a diallyl phthalate monomer, it will not be limited. As the above-mentioned diallyl phthalate monomer, an orthoobject, an isoobject, and a tele object are mentioned, for example. Although not limited especially as a catalyst of a hardening reaction, concomitant use of t-butyl par benzoate and di-t-butyl peroxide is preferred, for example.

[0047]As the above-mentioned silicone resin, especially if a silicon-silicon bond, a silicon-carbon to carbon bond, a siloxane bond, or silicon-nitrogen combination is included in a chain, it will not be limited, but specifically, a polysiloxane, polycarbosilane, polysilazane, etc. are mentioned, for example.

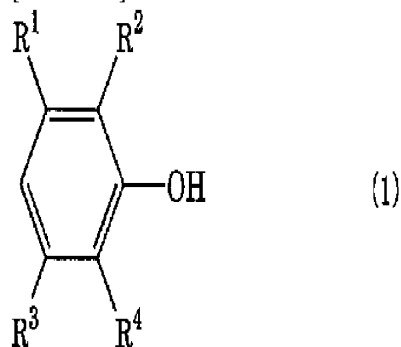
[0048]As the above-mentioned benzoxazine resin, especially if obtained by ring opening polymerization of an oxazine ring of a benzoxazine monomer, it will not be limited. What it was not limited especially as the above-mentioned benzoxazine monomer, for example, functional groups, such as a phenyl group, a methyl group, and a cyclohexyl group, combined with nitrogen of an oxazine ring is mentioned.

[0049]It is not limited especially as the above-mentioned thermoplastics, but For example, polyphenylene ether system resin, Polyphenylene ether system resin by which functional group denaturation was carried out; Polyphenylene ether system resin or polyphenylene ether system resin by which functional group denaturation was carried out, A mixture of polyphenylene ether system resin, such as polystyrene system resin, or polyphenylene ether system resin by which functional group denaturation was carried out, and thermoplastics which may dissolve; Alicyclic hydrocarbon system resin, Thermoplastic polyimide system resin, polyether ether ketone (PEEK) system resin, Polyether sulfone resin, polyamidoimide system resin, polyester imide system resin, Polyester system resin, polyolefin system resin, polystyrene system resin, polyamide system resin, polyvinyl-acetal system resin, polyvinyl alcohol system resin, polyvinyl acetate system resin, poly(meta) acrylic ester system resin, polyoxymethylene system resin, etc. are mentioned. Polyphenylene ether system resin, polyphenylene ether system resin by which functional group denaturation was carried out especially, A mixture of polyphenylene ether system resin, or polyphenylene ether system resin and polystyrene system resin by which functional group denaturation was carried out, Alicyclic hydrocarbon system resin, thermoplastic polyimide system resin, polyether ether ketone system resin, polyether sulfone resin, polyamidoimide system resin, polyester imide system resin, etc. are used suitably. These thermoplastics may be used independently and two or more sorts may be used together.

[0050]The above-mentioned polyphenylene ether system resin is a polyphenylene ether homopolymer or a polyphenylene ether copolymer which consists of a repeating unit shown in a following formula (1).

[0051]

[Formula 1]



[0052]R₁, R₂, R₃, and R₄ express a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, or an alkoxyl group among the above-mentioned formula (1). These alkyl groups, the aralkyl group, the aryl group, and the alkoxyl group may be replaced by the functional group, respectively.

[0053] It is not limited especially as the above-mentioned polyphenylene ether homopolymer. For example, poly(2,6-dimethyl-1,4-phenylene) ether, Poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, Poly(2-ethyl-6-n-propyl-1,4-phenylene) ether, Poly(2,6-di-n-propyl-1,4-phenylene) ether, Poly(2-ethyl-6-n-butyl-1,4-phenylene) ether, poly(2-ethyl-6-isopropyl-1,4-phenylene) ether, poly(2-methyl-6-hydroxyethyl 1,4-phenylene) ether, etc. are mentioned.

[0054] It is not limited especially as the above-mentioned polyphenylene ether copolymer. For example, a copolymer which contains some alkyl 3 substitution phenol, such as 2,3,6-trimethyl phenol, etc. in a repeating unit of the above-mentioned polyphenylene ether homopolymer, A copolymer etc. in which the graft copolymerization of one sort of styrene system monomers, such as styrene, alpha-methylstyrene, and vinyltoluene, or the two sorts or more was further carried out to these polyphenylene ether copolymers are mentioned. These polyphenylene ether system resin may be used independently, respectively, and two or more sorts of things from which a presentation, an ingredient, a molecular weight, etc. differ may be used together.

[0055] That etc. in which it was not limited especially as polyphenylene ether system resin by which functional group denaturation was carried out [above-mentioned], for example, the above-mentioned polyphenylene ether system resin denaturalized by one sort of functional groups, such as a maleic anhydride group, a glycidyl group, an amino group, and an allyl group, or two sorts or more are mentioned. These polyphenylene ether system resin by which functional group denaturation was carried out may be used independently, and two or more sorts may be used together. If polyphenylene ether system resin by which functional group denaturation was carried out [above-mentioned] is used as thermoplastics, the dynamic physical properties of a charge of insulating-substrate material of this invention, heat resistance, dimensional stability, etc. can be raised more by carrying out crosslinking reaction.

[0056] It is not limited especially as a mixture of the above-mentioned polyphenylene ether system resin, or polyphenylene ether system resin and polystyrene system resin by which functional group denaturation was carried out, For example, the above-mentioned polyphenylene ether system resin or polyphenylene ether system resin by which functional group denaturation was carried out [above-mentioned], Styrene homopolymer; a mixture with polystyrene system resin, such as one sort of styrene system monomers, such as styrene, alpha-methylstyrene and ethylstyrene, t-butylstyrene, and vinyltoluene, or two sorts or more of copolymer; styrene system elastomers, etc. are mentioned. The above-mentioned polystyrene system resin may be used independently, and two or more sorts may be used together. A mixture of these polyphenylene ether system resin, or polyphenylene ether system resin and polystyrene system resin by which functional group denaturation was carried out may be used independently, and two or more sorts may be used together.

[0057] Especially if it is hydrocarbon system resin which has an annular hydrocarbon group in a polymers chain as the above-mentioned alicyclic hydrocarbon system resin, it will not be limited, for example, a homopolymer or a copolymer of cyclic olefin, i.e., a norbornene system monomer, etc. is mentioned. These alicyclic hydrocarbon system resin may be used independently, and two

or more sorts may be used together.

[0058]It is not limited especially as the above-mentioned cyclic olefin, but For example, norbornene, Methano octahydronaphthalene, dimethano octahydronaphthalene, Dimethano dodecahydroanthracene, dimethanodecahydronaliumanthracene, Trimethano dodecahydroanthracene, a dicyclopentadiene, a 2,3-dihydrocyclopentadiene, Methano octahydro benzoindene, dimethano octahydro benzoindene, methano DEKAHIDORO benzoindene, dimethano DEKAHIDORO benzoindene, a methano octahydro fluorene, dimethano octahydro fluorenes, these substitution products, etc. are mentioned. These cyclic olefin may be used independently and two or more sorts may be used together.

[0059]It is not limited especially as a substituent in substitution products, such as the above-mentioned norbornene, for example, publicly known hydrocarbon groups and polar groups, such as an alkyl group, an alkylidene group, an aryl group, a cyano group, an alkoxy carbonyl group, a pyridyl group, and a halogen atom, are mentioned. These substituents may be used independently and two or more sorts may be used together.

[0060]It is not limited especially as substitution products, such as the above-mentioned norbornene, but For example, 5-methyl-2-norbornene, 5,5-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-butyl-2-norbornene, 5-ethylidene-2-norbornene, 5-carbomethoxy-2-norbornene, 5-cyano 2-norbornene, 5-methyl-5-carbomethoxy-2-norbornene, 5-phenyl-2-norbornene, 5-phenyl-5-methyl-2-norbornene, etc. are mentioned. Substitution products, such as these norbornene, may be used independently and two or more sorts may be used together.

[0061]As what is marketed among the above-mentioned alicyclic hydrocarbon system resin, trade name "ARTON" series by a J S R (JSR) company, trade name "ZEONOA" series by Nippon Zeon Co., Ltd., trade name "Abel" series by Mitsui Chemicals, Inc., etc. are mentioned, for example.

[0062]Polyetherimide resin which is not limited especially as the above-mentioned thermoplastic polyimide system resin, for example, has imide bonding and an ether bond in a molecule main chain, Polyamide imide resin which has imide bonding and an amide bond in a molecule main chain, polyester imide resin which has imide bonding and an ester bond in a molecule main chain, etc. are mentioned. These thermoplastic polyimide system resin may be used independently, and two or more sorts may be used together.

[0063]It is not limited especially as the above-mentioned polyether ether ketone resin, for example, what is produced by carrying out the polycondensation of dihalogeno benzophenone and the hydroquinone is mentioned.

[0064]The above-mentioned varnish composition contains a sheet silicate. In this specification, a sheet silicate may mean a stratified silicate mineral which has a convertibility metallic cation between layers, may be a natural product, and may be a compound. It is not limited especially as the above-mentioned sheet silicate, for example, smectite system argillite, such as montmorillonite, hectorite, saponite, beidellite, a stevensite, and nontronite, swelling mica, a vermiculite, halloysite, etc. are mentioned. Especially, at least one sort chosen from a group which consists of montmorillonite, hectorite, and swelling mica is used suitably. These sheet

silicates may be used independently and two or more sorts may be used together.

[0065]Although not limited especially as crystal form of the above-mentioned sheet silicate, a minimum with preferred average length 0.01 micrometer, A minimum in which a maximum of 3 micrometers and thickness is preferred 0.001 micrometer and a maximum 1 micrometer, A desirable minimum of an aspect ratio is 20, a maximum is 500, and, as for 0.01 micrometer and a maximum, 0.05 micrometer and a maximum are [more desirable minimum of average length / more desirable minimum of 2 micrometers and thickness / 50 and a maximum of a more desirable minimum of 0.5 micrometer and an aspect ratio] 200.

[0066]As for the above-mentioned sheet silicate, it is preferred that the shape anisotropy effect defined by following formula (2) is large. By using a large sheet silicate of the shape anisotropy effect, a charge of insulating-substrate material of this invention has outstanding dynamic physical properties.

[0067]

[Equation 1]

形状異方性効果＝薄片状結晶の積層面の表面積／薄片状結晶の積層側面の表面積 (2)

[0068]With the convertibility metallic cation which exists between the layers of the above-mentioned sheet silicate. Metal ions which exist in the flaky crystal surface of a sheet silicate, such as sodium and calcium, are meant, and since these metal ions have cation exchange nature with a cationic substance, they can insert various substances which have cationicity between the crystal layers of the above-mentioned sheet silicate (intercalation).

[0069]Although not limited especially as cation exchange capacity of the above-mentioned sheet silicate, desirable minimums are 50-mm equivalent weight /100g, and maximums are 200-mm equivalent weight /100g. Since quantity of a cationic substance intercalated by cation exchange between crystal layers of a sheet silicate will decrease if it is 50 mm equivalent weight / less than [100g], between crystal layers may not fully be un-polarized (hydrophobing). If 200-mm equivalent weight / 100g is exceeded, associative strength between crystal layers of a sheet silicate will become firm too much, and a crystal flake will become difficult to exfoliate.

[0070]As the above-mentioned sheet silicate, it is preferred by carrying out a chemical treatment to improve dispersibility to inside of resin which consists of thermosetting resin and/or thermoplastics. This sheet silicate is also hereafter called organicity-ized sheet silicate. As the above-mentioned chemical treatment, it can carry out by a chemical modification (1) method - a chemical modification (6) method which are shown below, for example. These chemical modification methods may be used independently and two or more sorts may be used together.

[0071]The above-mentioned chemical modification (1) method is also called cation exchange method by a cationic surface-active agent, and specifically, When obtaining a charge of insulating-substrate material of this invention using low polar resin, such as polyphenylene ether resin, it is the method of carrying out cation exchange of between layers of a sheet silicate, and carrying out hydrophobing with a cationic surface-active agent, beforehand. By carrying out hydrophobing of between layers of a sheet silicate beforehand, the compatibility of a sheet

silicate and low polar resin can increase, and micro-disperse of the sheet silicate can be uniformly carried out by inside of low polar resin.

[0072]It is not limited especially as the above-mentioned cationic surface-active agent, for example, quarternary ammonium salt, the 4th class phosphonium salt, etc. are mentioned. Especially, since hydrophobing of between crystal layers of a sheet silicate can fully be carried out, quarternary ammonium salt which has a with a carbon numbers of six or more alkyl chain containing with a carbon numbers of six or more alkyl ammonium ion is used suitably.

[0073]It is not limited especially as the above-mentioned quarternary ammonium salt, but For example, trimethyl alkyl ammonium salt, Triethyl alkyl ammonium salt, tributyl alkyl ammonium salt, Dimethyl dialkyl ammonium salt, dibutyl dialkyl ammonium salt, Methylbenzyl dialkyl ammonium salt, dibenzyl dialkyl ammonium salt, A trialkyl methylammonium salt, a trialkyl ethylammonium salt, Trialkyl butylammonium salt, quarternary ammonium salt which has an aromatic ring, Quarternary ammonium salt of aromatic amine origin of trimethyl phenyl ammonium etc., Dialkyl quarternary ammonium salt which has two polyethylene-glycol chains, Dialkyl quarternary ammonium salt which has two polypropylene-glycol chains, trialkyl quarternary ammonium salt which has one polyethylene-glycol chain, trialkyl quarternary ammonium salt which has one polypropylene-glycol chain, etc. are mentioned. Lauryl trimethylammonium salt, stearyl trimethylammonium salt especially, A trioctyl methylammonium salt, a distearyl dimethylbenzylammonium salt, a JI hardening beef tallow dimethylannmonium salt, distearyl dibenzylammonium salt, the N-polyoxyethylene N-lauryl N, N-dimethylannmonium salt, etc. are preferred. These quarternary ammonium salt may be used independently and two or more sorts may be used together.

[0074]It is not limited especially as the above-mentioned 4th class phosphonium salt, but For example, a dodecyl triphenyl phosphonium salt, A methyltriphenylphosphonium salt, lauryl trimethyl phosphonium salt, Stearyl trimethyl phosphonium salt, trioctyl phosphonium salt, trioctyl methyl phosphonium salt, distearyl dimethyl phosphonium salt, distearyl dibenzyl phosphonium salt, etc. are mentioned. The 4th class phosphonium salt of such may be used independently, and two or more sorts may be used together.

[0075]The above-mentioned chemical modification (2) method is the method of carrying out the chemical treatment of the large functional group of chemical compatibility with a functional group or a hydroxyl group which can carry out the chemical bond of the hydroxyl group which exists in a crystal surface of an organicity-ized sheet silicate by which the chemical treatment was carried out by a chemical modification (1) method to a hydroxyl group with a compound which it has in one or more molecular terminals.

[0076]It is not limited especially as a large functional group of chemical compatibility with a functional group or a hydroxyl group which can carry out a chemical bond to the above-mentioned hydroxyl group, for example, an alkoxy group, a glycidyl group, a carboxyl group (a dibasicity acid anhydride is also included), a hydroxyl group, an isocyanate group, an aldehyde group, etc. are mentioned. A silane compound, a titanate compound, a glycidyl compound, carboxylic acid, alcohols, etc. which are not limited especially as a compound which has a large

functional group of chemical compatibility with a compound or a hydroxyl group which has a functional group which can carry out a chemical bond to the above-mentioned hydroxyl group, for example, have the above-mentioned functional group are mentioned. These compounds may be used independently and two or more sorts may be used together.

[0077]It is not limited especially as the above-mentioned silane compound, but For example, vinyltrimethoxysilane, Vinyltriethoxysilane, vinyltris (beta-methoxyethoxy) Silane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl triethoxysilane, gamma-aminopropyl methyldiethoxysilane, gamma-aminopropyl dimethylethoxy silane, Methyl triethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, Hexyl trimethoxysilane, hexyl triethoxysilane, N-beta-(aminoethyl) gamma-aminopropyl trimethoxysilane, N-beta-(aminoethyl) gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl) gamma-aminopropyl methyl dimethoxysilane, Octadecyltrimethoxysilane, octadecyl triethoxysilane, Gamma-methacryloxypropylmethyldimethoxysilane, gamma-methacryloxypropylmethyldiethoxysilane, gamma-methacryloxypropyl trimethoxy silane, gamma-methacryloxypropyl triethoxysilane, etc. are mentioned. These silane compounds may be used independently and two or more sorts may be used together.

[0078]The above-mentioned chemical modification (3) method is the method of carrying out a chemical treatment with a functional group or a hydroxyl group which can carry out the chemical bond of the hydroxyl group which exists in a crystal surface of an organically-ized sheet silicate by which the chemical treatment was carried out by a chemical modification (1) method to a hydroxyl group, a large functional group of chemical compatibility, and a compound which has a reactive functional group in one or more molecular terminals.

[0079]The above-mentioned chemical modification (4) method is the method of carrying out the chemical treatment of the crystal surface of an organically-ized sheet silicate by which the chemical treatment was carried out by a chemical modification (1) method with a compound which has anionic surface activity.

[0080]As a compound which has the above-mentioned anionic surface activity, It will not be limited especially if the chemical treatment of the sheet silicate can be carried out by an ionic interaction, For example, lauryl acid sodium, sodium stearate, sodium oleate, fatty alcohol sulfate, the 2nd class fatty alcohol sulfate, unsaturated alcohol sulfuric ester salt, etc. are mentioned. These compounds may be used independently and two or more sorts may be used together.

[0081]The above-mentioned chemical modification (5) method is the method of carrying out a chemical treatment with a compound which has one or more reactive functional groups among compounds which have the above-mentioned anionic surface activity in addition to an anion part in a chain.

[0082]The above-mentioned chemical modification (6) method to an organically-ized sheet silicate by which the chemical treatment was carried out by a method of either a chemical modification (1) method - a chemical modification (5) method. It is the method of using resin which has a

functional group in which a sheet silicate and a reaction like maleic anhydride modified-polyphenylene-ether system resin are possible, for example as resin which consists of thermosetting resin and/or thermoplastics.

[0083] 0.1 weight sections and maximums are 100 weight sections to resin 100 weight section which a minimum of loadings of the above-mentioned sheet silicate becomes from thermosetting resin and/or thermoplastics. An improvement effect of fire retardancy or dynamic physical properties becomes it small that they are less than 0.1 weight sections. If 100 weight sections are exceeded, density of a charge of insulating substrate material of this invention becomes high, and since a mechanical strength also falls, it will become lacking in practicality. A minimum with preferred loadings is one weight section, and maximums are 50 weight sections. If it is less than one weight section, when a charge of insulating substrate material of this invention is fabricated thinly, sufficient fire-resistant effect may not be acquired. When 50 weight sections are exceeded, a moldability may fall. More desirable minimums of loadings are five weight sections, and maximums are 20 weight sections. There is no field which becomes being five to 20 weight section with a problem in dynamic physical-properties and process fitness, and sufficient fire retardancy is acquired.

[0084] A method to which a varnish composition is made to foam with a foaming agent after not being limited especially as a method of distributing a sheet silicate, into the above-mentioned varnish composition, for example, mixing the method; resin, a sheet silicate, and an organic solvent using an organicity-ized sheet silicate with a conventional method; a method of using a dispersing agent, etc. are mentioned. By using these dispersion methods, a sheet silicate can be distributed more uniformly and minutely in a varnish composition.

[0085] A method to which the above-mentioned varnish composition is made to foam with a foaming agent uses energy by foaming for distribution of a sheet silicate. It is not limited especially as the above-mentioned foaming agent, for example, a gas-like foaming agent, an easy-volatility liquefied foaming agent, a decomposed type solid state foaming agent, etc. are mentioned. These foaming agents may be used independently and two or more sorts may be used together.

[0086] It is not limited especially as a method to which the above-mentioned varnish composition is made to foam with a foaming agent, For example, a method of making this gas-like foaming agent evaporate within the above-mentioned varnish composition, and forming foam, after impregnating a varnish composition with a gas-like foaming agent under high voltage; A decomposed type foaming agent is made to contain beforehand between layers of a sheet silicate, A method of making heating decompose the decomposed type foaming agent, and forming foam, etc. are mentioned.

[0087] The above-mentioned varnish composition contains an organic solvent. It is not limited especially as the above-mentioned organic solvent, but For example, hexane, cyclohexane, A carbon tetrachloride, chloroform, dichloromethane, diethylether, 1, 2-dimethoxyethane, A tetrahydrofuran, 1,4-dioxane, ethyl acetate, N.N-dimethylformamide, Hexamethylphosphoramide, acetic acid, acetone, methyl ethyl ketone, Methanol, ethanol,

nitromethane, dimethyl sulfoxide, sulfolane, benzene, toluene, xylene, naphthalene, chlorobenzene, an anisole, diphenyl ether, pyridine, nitrobenzene, etc. are mentioned. Especially, for distributing a sheet silicate, a polar organic solvent is preferred, and it is a more desirable aprotic polar organic solvent. An aprotic polar organic solvent means a polar organic solvent without hydrogen suitable for formation of a strong hydrogen bond, and, specifically, acetone, methyl ethyl ketone, acetonitrile, dimethyl sulfoxide, n,n-dimethylformamide, hexamethylphosphoramide, etc. are mentioned. These organic solvents may be used independently and two or more sorts may be used together.

[0088] Although loadings of the above-mentioned organic solvent differ in the optimum amount according to loadings of the above-mentioned resin or a sheet silicate, and a kind of organic solvent, Generally the one where resin concentration and sheet silicate concentration are lower is preferred, specifically, minimums to resin 100 weight section which consists of at least one sort of thermosetting resin and/or thermoplastics are 30 weight sections, and maximums are 1000 weight sections. Viscosity of a solution which becomes being less than 30 weight sections from a resin varnish constituent is too high, and the cast is difficult. When 1000 weight sections are exceeded, when carrying out the cast of the solution, poor coating may arise, or thick film-ization may become difficult. Minimums with preferred loadings of the above-mentioned organic solvent are 100 weight sections, a more desirable minimum is 150 or more weight sections, and being mostly blended rather than a sheet silicate is preferred.

[0089] The above-mentioned varnish composition may contain fire retardant which does not contain a halogen system constituent, when a charge of insulating-substrate material of this invention contains fire retardant which does not contain a halogen system constituent. Although it is preferred to contain fire retardant which does not contain a halogen system constituent as for a charge of insulating-substrate material of this invention, it does not care about it that a small amount of halogen mixes for convenience' sake on a manufacturing process of fire retardant etc.

[0090] It is not limited especially as the above-mentioned fire retardant, but For example, aluminium hydroxide, Magnesium hydroxide, a dawsonite, an ulmin calcium oxide, 2 hydration gypsum, metal hydroxide [, such as calcium hydroxide,]; -- metallic-oxide; -- Lynn system compound [, such as red phosphorus and ammonium polyphosphate,]; -- melamine. Stratified double hydrates, such as nitrogen system compounds, such as a melamine derivative which performed a surface treatment to melamine cyanurate, melamine isocyanurate, melamine phosphate, and these, a fluoro-resin, silicone oil, and a hydrotalcite; silicone acrylic composite rubber etc. are mentioned. Especially, metal hydroxide and a melamine derivative are preferred. Also in the above-mentioned metal hydroxide, especially magnesium hydroxide and aluminium hydroxide are preferred, and a surface treatment may be performed by finishing agent of various kinds [these]. It is not limited especially as the above-mentioned finishing agent, for example, a silane coupling agent, a titanate system coupling agent, a PVA system finishing agent, an epoxy system finishing agent, etc. are mentioned. These fire retardant may be used independently and two or more sorts may be used together.

[0091] When using metal hydroxide as the above-mentioned fire retardant, 0.1 weight sections

and maximums are 100 weight sections to resin 100 weight section which a minimum with preferred loadings of metal hydroxide becomes from thermosetting resin and/or thermoplastics. If it is less than 0.1 weight sections, the flameproofing effect may not fully be acquired. When 100 weight sections are exceeded, density (specific gravity) of insulating-substrate material of this invention may become high too much, and practicality may become scarce, or pliability and ductility may fall extremely. More desirable minimums are five weight sections and maximums are 80 weight sections. If it is less than five weight sections, when insulating-substrate material of this invention is made thin, sufficient flameproofing effect may not be acquired. When 80 weight sections are exceeded, dynamic physical properties may fall or defects, such as bulging in a process of performing high temperature processing, may increase in number. Desirable minimums are ten weight sections and maximums are 70 weight sections. There is no field which becomes being the range of ten to 70 weight section with a problem by dynamic physical properties, an electric property, process fitness, etc., and sufficient fire retardancy is revealed.

[0092]When using a melamine derivative as the above-mentioned fire retardant, 0.1 weight sections and maximums are 100 weight sections to resin 100 weight section which a minimum with preferred loadings of a melamine derivative becomes from thermosetting resin and/or thermoplastics. If it is less than 0.1 weight sections, the flameproofing effect may not fully be acquired. When 100 weight sections are exceeded, dynamic physical properties, such as pliability and ductility, may fall extremely. More desirable minimums are five weight sections and maximums are 70 weight sections. If it is less than five weight sections, when a charge of insulating-substrate material of this invention is made thin, sufficient flameproofing effect may not be acquired. When 70 weight sections are exceeded, dynamic physical properties, such as pliability and ductility, may fall extremely. Desirable minimums are ten weight sections and maximums are 50 weight sections. There is no field which becomes being the range of ten to 50 weight section with a problem by dynamic physical properties, an electric property, process fitness, etc., and sufficient fire retardancy is revealed.

[0093]The above-mentioned varnish composition may contain the above-mentioned additive agent, when an additive agent is blended with a charge of insulating-substrate material of this invention for the purpose of reforming the characteristic in the range which does not check technical-problem achievement of this invention. It is not limited especially as the above-mentioned additive agent, for example, thermoplastic elastomer, cross linked rubber, oligomer, a nucleating agent, an antioxidant (antiaging agent), a thermostabilizer, light stabilizer, an ultraviolet ray absorbent, lubricant, a fire-resistant auxiliary agent, a spray for preventing static electricity, an antifogger, a bulking agent, a softener, a plasticizer, colorant, etc. are mentioned. These may be used independently, respectively and two or more sorts may be used together.

[0094]It is not limited especially as the above-mentioned thermoplastic elastomer, for example, a styrene system elastomer, an olefin system elastomer, a urethane system elastomer, a polyester system elastomer, etc. are mentioned. In order to improve compatibility with resin, functional group denaturation of these thermoplastic elastomer may be carried out. These thermoplastic elastomer may be used independently and two or more sorts may be used together.

[0095]It is not limited especially as the above-mentioned cross linked rubber, for example, polyisoprene rubber, butadiene rubber, 1,2-polybutadiene, a styrene butadiene rubber, nitrile rubber, isobutylene isoprene rubber, ethylene-propylene rubber, silicone rubber, urethane rubber, etc. are mentioned. In order to improve compatibility with resin, it is preferred to carry out functional group denaturation of such cross linked rubbers. It is not limited especially as cross linked rubber which carried out [above-mentioned] functional group denaturation, for example, epoxy denaturation butadiene rubber, epoxy denaturation nitrile rubber, etc. are mentioned. Such cross linked rubbers may be used independently and two or more sorts may be used together.

[0096]It is not limited especially as the above-mentioned oligomer, for example, maleic anhydride modified polyethylene oligomer etc. are mentioned. These oligomer may be used independently and two or more sorts may be used together.

[0097]A charge of insulating-substrate material of this invention is obtained by drying a resin varnish constituent. It is not limited especially as a method of manufacturing a charge of insulating-substrate material of this invention. For example, an every place fixed quantity of one sort or two sorts or more of additive agents blended resin which consists of at least one sort of thermosetting resin and/or thermoplastics, a sheet silicate, an every place fixed quantity of an organic solvent, and if needed is mixed under ordinary temperature or heating, How to dry this resin varnish constituent and to remove an organic solvent after producing a resin varnish constituent; A masterbatch which blended and kneaded a sheet silicate more than the specified quantity to the above-mentioned resin beforehand is produced, An every place fixed quantity of one sort or two sorts or more of additive agents blended the remainder of the specified quantity of this masterbatch and the above-mentioned resin, an organic solvent, and if needed is mixed under ordinary temperature or heating, After producing a resin varnish constituent, the masterbatch method for drying this resin varnish constituent and removing an organic solvent, etc. are mentioned.

[0098]A method of mixing a sheet silicate and an organic solvent beforehand, and also adding resin or resin used as a solution, and mixing as the method of the above-mentioned mixing, is common, and it is preferred to use shooting star type agitating equipment, a homogenizer, and a mechanochemical agitator.

[0099]In using thermoplastics as the above-mentioned resin, For example, by kneading a monomer and a sheet silicate of thermoplastics and polymerizing the above-mentioned monomer using a sheet silicate containing a polymerization catalyst (polymerization initiator) like transition metal complexes, A method of a polymerization of thermoplastics and manufacture of a charge of insulating-substrate material of this invention being simultaneously put in block, and performing them may be used.

[0100]In using thermosetting resin as the above-mentioned resin, For example, by kneading a monomer of thermosetting resin, a sheet silicate, and an organic solvent, and stiffening the above-mentioned monomer using a sheet silicate containing a hardening agent (cross linking agent) like amines (bridge construction), A method of removal of an organic solvent, and hardening (bridge construction) of thermosetting resin and manufacture of a charge of insulating-substrate material

of this invention being simultaneously put in block, and performing it may be used.

[0101]By drying the above-mentioned resin varnish constituent and obtaining a charge of insulating-substrate material of this invention, in a charge of insulating-substrate material of this invention, a sheet silicate, Average interlaminar distance of a field measured by a wide angle X diffraction measuring method (001) is not less than 3 nm, and all layered products are distributed as a layered product of five or less layers in part. By the above-mentioned average interlaminar distance of the above-mentioned sheet silicate being not less than 3 nm, and distributing a part or all of a sheet silicate as a layered product of five or less layers, An interfacial area of resin which consists of thermosetting resin and/or thermoplastics, and a sheet silicate is large enough, And distance between flaky crystals of a sheet silicate will become moderate, sufficient effect by distribution of a sheet silicate is acquired, and bigger dynamic physical properties than a time of using the usual inorganic filler and a fire-resistant improvement effect are acquired in a charge of insulating-substrate material of this invention.

[0102]A desirable maximum of the above-mentioned average interlaminar distance is 5 nm. Since it will become weaker so that a crystal flake of a sheet silicate dissociates for every layer and can disregard an interaction if it exceeds 5 nm, film formation at the time of combustion becomes late, and fire-resistant improvement may not fully be obtained. In this specification, average interlaminar distance of a sheet silicate means an average of distance between layers [flaky crystal / of a sheet silicate / layer / the bottom] of a case wholly, and it can compute by an X diffraction peak and transmission electron microscope photography, i.e., a wide angle X diffraction measuring method.

[0103]That a part or all of the above-mentioned sheet silicate distributes as a layered product of five or less layers means that an interaction between flaky crystals of a sheet silicate can weaken, and a part or all of a layered product of a flaky crystal is specifically distributing. It is more preferred that not less than 10% of sheet silicates are distributing as a layered product of five or less layers, and not less than 20% of sheet silicates are distributing as a layered product of five or less layers preferably. A rate of a sheet silicate currently distributed as a layered product of five or less layers, It is computable from a following formula (3) by measuring the number of layers Y of a layered product currently distributed as the number X of total layers of a layered product of a sheet silicate which expands a charge of insulating-substrate material of this invention by 50,000 to 100,000 times with a transmission electron microscope, observes it, and can be observed in a definite area, and a layered product of five or less layers.

[0104]

[Equation 2]

5層以下の積層体として分散している層状珪酸塩の割合 (%) = $(Y/X) \times 100$ (3)

[0105]in order to acquire the effect by distribution of a sheet silicate as the number of laminations in the layered product of a sheet silicate, it is preferred that they are five or less layers, it is three or less layers more preferably, and is one layer still more preferably.

[0106]Since the interaction of resin and the surface of a sheet silicate becomes large, according to

the interfacial area of the above-mentioned resin and a sheet silicate being sufficiently large the charge of insulating-substrate material of this invention, In addition to melt viscosity increasing and a moldability improving, dynamic physical properties, such as an elastic modulus, improve in the large temperature range from ordinary temperature to an elevated temperature, also at the elevated temperature more than the glass transition temperature of resin, or the melting point, dynamic physical properties can be held and the coefficient of linear expansion at the time of an elevated temperature can also be stopped low. Although this reason is not clear, since the sheet silicate of a micro-disperse state is acting as a kind of point constructing [false] a bridge, it is thought also in the field more than a glass transition point or the melting point that these physical properties are revealed. On the other hand, since the distance between the flaky crystals of the above-mentioned sheet silicate is moderate, the charge of insulating-substrate material of this invention tends to form the sintered compact which the flaky crystal of a sheet silicate moves and can serve as a fire-resistant tunic at the time of combustion. Since this sintered compact is formed in the early stage at the time of combustion, the combustible gas emitted by combustion can be intercepted it not only intercepts supply of oxygen from the external world, but, and the charge of insulating-substrate material of this invention reveals the outstanding fire retardancy.

[0107] Since a gas molecule is diffused bypassing a sheet silicate when it is easy to diffuse a direction of a gas molecule far and it diffuses inside of resin compared with an inorganic substance in the above-mentioned resin, gas barrier property of a charge of this invention of insulating-substrate material improves. Barrier property [/ in addition to a gas molecule] improves similarly, and solvent resistance, moisture absorption resistance, absorptivity-proof, etc. improve. Thereby, migration of copper from a copper circuit in a multilayer printed wiring board can be controlled, for example. It can also be controlled that a minute amount additive in resin carries out bleed out to the surface, and fault of poor plating occurs.

[0108] By drying the above-mentioned resin varnish constituent and obtaining a charge of insulating-substrate material of this invention, a charge of insulating-substrate material of this invention, Yield stress at the time of compressing combustion residue burned by heating for 30 minutes on radiation heating conditions of 50 kW/m^2 by speed 0.1 cm/s can be set to 4.9 or more kPa. Collapse of combustion residue does not take place that the above-mentioned yield stress is 4.9 or more kPa by minute power, and sufficient fire retardancy is acquired. That is, in order to make fire retardancy into sufficient thing, a sintered compact needs to hold the shape till a burn out, and it is necessary to fully reveal a function as a fire-resistant tunic. They are 15.0 or more kPa preferably. The above-mentioned burning test can be done by being based on ASTM E 1354.

[0109] A charge of insulating-substrate material of this invention by drying a resin varnish constituent containing resin, a sheet silicate, and an organic solvent which consist of at least one sort of thermosetting resin, and/or thermoplastics, and being manufactured, Since swelling depressor effect accompanying a nucleating effect of a sheet silicate in the rise effect of glass transition temperature by restraint of a chain or heat-resistant deformation temperature and crystal formation, damp-proof improvement, etc., etc. are acquired, it excels in dynamic physical properties, transparency, moisture resistance, heat resistance, dimensional stability, etc., and has

the low heat ray rate of expansion. Since a sintered compact by a sheet silicate is formed at the time of combustion, shape of combustion residue is held, and the charge of insulating-substrate material of this invention can prevent the spread of a fire, and reveals outstanding fire retardancy. It is compatible in high dynamic physical properties etc. and high fire retardancy by combining with non halogen fire retardant, such as metal hydroxide, also considering environment. A charge of insulating-substrate material of this invention is processible into a thin Plastic solid from giving dynamic physical properties etc. which were excellent even if a sheet silicate did not blend so much like the usual inorganic bulking agent. A charge of insulating-substrate material of this invention which carried out thinning corresponding to densification of a multilayer printed board and slimming down, Excelling in fire retardancy, dynamic physical properties, a high temperature physical property, heat resistance, dimensional stability, solvent resistance, moisture absorption resistance, gas barrier property, etc., a yield of a multilayer printed board manufactured through a multi process improves substantially by using a charge of insulating-substrate material of this invention which has the high quality in which the above-mentioned characteristic has been improved.

[0110]Although not limited especially as a use of a charge of insulating-substrate material of this invention, it is used, for example by fabricating suitably for an insulating substrate, a laminate sheet, a printed circuit board, copper foil with resin, copper clad laminate, a polyimide film, a film for TAB, prepreg, a core layer, a buildup layer of a multilayer substrate, etc. A laminate sheet, a printed circuit board, copper foil with resin and copper clad laminate which use a charge of insulating-substrate material, a polyimide film, a film for TAB, and prepreg of this this invention are also one of this inventions.

[0111]It extrudes, after not being limited especially as the method of the above-mentioned shaping, for example, carrying out melt kneading with an extrusion machine, An extrusion method fabricated to film state using a T die, a circular die, etc.; After dissolving or distributing solvents, such as an organic solvent, A casting molding method which is cast and is fabricated to film state; a dipping molding method etc. which carry out dipping of cross state or a nonwoven fabric state substrate which consists of inorganic materials and organic polymer, such as glass, and fabricate it to film state are mentioned into a varnish dissolved, or distributed and obtained to solvents, such as an organic solvent. Especially, in order to attain slimming down of a multilayer substrate, an extrusion method and a casting molding method are preferred. It is not limited especially as a substrate used in the above-mentioned dipping molding method, for example, glass fabrics, an aramid fiber, poly para-phenylene benzoxazol textiles, etc. are mentioned.

[0112]A laminate sheet, a printed circuit board, copper foil with resin, copper clad laminate, a polyimide film, a film for TAB, and prepreg of this invention, A charge of insulating-substrate material of this invention is used, and since, it excels in dynamic physical properties, a high temperature physical property, dimensional stability, solvent resistance, moisture absorption resistance, gas barrier property, heat resistance, etc., and has the outstanding fire retardancy especially by a shape retention effect at the time of combustion.

[0113]

[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples.

[0114](Example 1) a bisphenol A type epoxy resin (the Dow Chemical Japan make.) D.E. R.331L) 45 weight sections and solid epoxy resin (the Tohto Kasei Co., Ltd. make.) epoxy resin composition 90 weight section which consists of YP55 45 weight section, and dicyandiamide (the product made by ADEKA.) ADEKA hardener EH-3636AS3.15 weight section and denaturation imidazole (the product made by ADEKA.) ADEKA hardener EH-3366S1.35 weight section and the synthetic hectorite (the CO-OP CHEMICAL CO., LTD. make.) in which organicity-ized processing was performed with the trioctyl methylammonium salt as a sheet silicate After adding dimethylformamide (Wako Pure Chem make, best) 400 weight section to the beaker as Lucentite STN10 weight section and an organic solvent and agitating with an agitator for 1 hour, it defoamed and resin / sheet silicate solution was obtained. Subsequently, where the obtained resin / sheet silicate solution are applied on the sheet of the state or polyethylene terephthalate put into the mold, after removing a solvent, 2 mm in thickness and the 100-micrometer tabular Plastic solid which heat at 110 ** for 3 hours, and also heat for 30 minutes, make it harden at 170 **, and consist of a charge of insulating-substrate material were produced.

[0115](Example 2) As an organic solvent, 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced like Example 1 instead of dimethylformamide except having used methyl ethyl ketone (the Wako Pure Chem make, best).

[0116](Example 3) Instead of being the synthetic hectorite in which organicity-ized processing was performed with the trioctyl methylammonium salt as a sheet silicate, Organicity-ized processing using the given natural montmorillonite (the Hojun Yoko Co., Ltd. make, New S-Ben D) by distearyl dimethyl quarternary ammonium salt as an organic solvent, Instead of dimethylformamide, 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced like Example 1 except having used the tetrahydrofuran (the Wako Pure Chem make, best).

[0117](Example 4) phenol novolak type epoxy resin (the Dainippon Ink & Chemicals, Inc. make.) N-770) 72 weight sections and triazine structure content phenol novolak resin (the Dainippon Ink & Chemicals, Inc. make.) Epoxy resin composition 100 weight section which consists of EXB-9820 28 weight section, the synthetic hectorite (the CO-OP CHEMICAL CO., LTD. make.) in which organicity-ized processing was performed with the trioctyl methylammonium salt as a sheet silicate After adding dimethylformamide (Wako Pure Chem make, best) 430 weight section to the beaker as Lucentite STN11 weight section and an organic solvent and agitating with an agitator for 1 hour, it defoamed and resin / sheet silicate solution was obtained. Subsequently, where the obtained resin / sheet silicate solution are applied on the sheet of the state or polyethylene terephthalate put into the mold, after removing a solvent, Heated at 110 ** for 3 hours, and also heat for 1 hour, it was made to harden at 170 **, and 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced.

[0118](Example 5) As an organic solvent, 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced like Example 4 instead of dimethylformamide except having used methyl ethyl ketone (the Wako Pure Chem make, best).

[0119](Example 6) a bisphenol A type epoxy resin (the Dow Chemical Japan make.) D.E. R.331L) 45 weight sections and solid epoxy resin (the Tohto Kasei Co., Ltd. make.) epoxy resin composition 90 weight section which consists of YP55 45 weight section, and dicyandiamide (the product made by ADEKA.) ADEKA hardener EH-3636AS3.15 weight section and denaturation imidazole (the product made by ADEKA.) ADEKA hardener EH-3366S1.35 weight section and the synthetic hectorite (the CO-OP CHEMICAL CO., LTD. make.) in which organicity-ized processing was performed with the trioctyl methylammonium salt as a sheet silicate as Lucentite STN10 weight section and fire retardant -- magnesium hydroxide (the Kyowa Chemical Industry Co., Ltd. make.) After adding dimethylformamide (Wako Pure Chem make, best) 500 weight section to the beaker as Kuisma 5J70 weight section and an organic solvent and agitating with an agitator for 1 hour, it defoamed and resin / sheet silicate solution was obtained. Subsequently, where the obtained resin / sheet silicate solution are applied on the sheet of the state or polyethylene terephthalate put into the mold, after removing a solvent, Heated at 110 ** for 3 hours, and also heat for 30 minutes, it was made to harden at 170 **, and 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced.

[0120](Example 7) phenol novolak type epoxy resin (the Dainippon Ink & Chemicals, Inc. make.) N-770) 72 weight sections and triazine structure content phenol novolak resin (the Dainippon Ink & Chemicals, Inc. make.) Epoxy resin composition 100 weight section which consists of EXB-9820 28 weight section, the synthetic hectorite (the CO-OP CHEMICAL CO., LTD. make.) in which organicity-ized processing was performed with the trioctyl methylammonium salt as a sheet silicate as Lucentite STN11 weight section and fire retardant -- magnesium hydroxide (the Kyowa Chemical Industry Co., Ltd. make.) After adding dimethylformamide (Wako Pure Chem make, best) 480 weight section to the beaker as Kuisma 5J45 weight section and an organic solvent and agitating with an agitator for 1 hour, it defoamed and resin / sheet silicate solution was obtained. Subsequently, where the obtained resin / sheet silicate solution are applied on the sheet of the state or polyethylene terephthalate put into the mold, after removing a solvent, Heated at 110 ** for 3 hours, and also heat for 1 hour, it was made to harden at 170 **, and 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced.

[0121](Comparative example 1) Instead of synthetic hectorite (CO-OP CHEMICAL CO., LTD. make, Lucentite STN) 10 weight section, 2 mm in thickness and the 100-micrometer tabular Plastic solid which consist of a charge of insulating-substrate material were produced like Example 1 except having used calcium carbonate 10 weight section with a mean particle diameter of 50 micrometers.

[0122]The performance of the charge of insulating-substrate material produced by the

<evaluation> examples 1, 2, 3, 4, 5, 6, and 7 and the comparative example 1 was evaluated about the following items. The result was shown in Table 1.

[0123](1) The average interlaminar distance X diffraction measuring device (the Rigaku make, RINT1100) of a sheet silicate is used, 2 theta of the diffraction peak obtained from diffraction of the lamination side of the sheet silicate in a 2-mm-thick tabular Plastic solid was measured, and d obtained by the diffraction type of the black of a following formula (4) by computing the spacing (001) d of a sheet silicate was made into average interlaminar distance (nm).

$$\lambda = 2d \sin \theta \quad (4)$$

lambda is 0.154 among the above-mentioned formula (4), and theta expresses an angle of diffraction.

[0124](2) A tabular Plastic solid with a rate thickness of 100 micrometers of the sheet silicate currently distributed as a layered product of five or less layers is observed by 100,000 times with a transmission electron microscope, The number of layers Y of the sheet silicate currently distributed by the number X of total layers of the layered product of a sheet silicate observable in a definite area and five layers or less was measured, and the rate (%) of the sheet silicate currently distributed as a layered product of five or less layers with the following formula (3) was computed.

[0125]

[Equation 3]

$$\text{5層以下の積層体として分散している層状珪酸塩の割合 (\%)} = (Y/X) \times 100 \quad (3)$$

[0126](3) The shape retentivity at the time of combustion, the maximum heat release rate, and the yield stress of combustion residue (tunic intensity)

Based on the inflammability test method of an ASTM E 1354"building material", the heat ray of 50 kW/m² was glared and burned with the corn calorimeter to the tabular Plastic solid with a thickness of 2 mm judged to 100 mm x 100 mm. At this time, the shape change of the tabular Plastic solid in combustion order was observed visually, and the maximum heat release rate (kW/m²) was measured. About combustion residue, it compressed by speed 0.1 cm/s using the intensity measurement device, and yield stress (tunic intensity) (kPa) was measured. The shape retentivity at the time of combustion was evaluated by the following judging standard about the shape change of the tabular Plastic solid before and behind combustion.

O : the shape change was very small.

x: The shape change was intense.

[0127]

[Table 1]

比較例1	45	45	—	400	3.15	1.35	10	—	—	×	650	1
ビスフェノールA型 エポキシ樹脂				ジメチル ホルムアミド	ジアンジンアミド	変性 イミダゾール	炭酸 カルシウム					

	実施例1		実施例2		実施例3		実施例4		実施例5		実施例6		実施例7	
	ビスフェノールA型エポキシ樹脂	45	ビスフェノールA型エポキシ樹脂	45	ビスフェノールA型エポキシ樹脂	45	ビスフェノールA型エポキシ樹脂	72	ビスフェノールA型エポキシ樹脂	72	ビスフェノールA型エポキシ樹脂	45	ビスフェノールA型エポキシ樹脂	72
樹脂	固形エポキシ樹脂	45	固形エポキシ樹脂	45	固形エポキシ樹脂	45	固形エポキシ樹脂	28	固形エポキシ樹脂	28	固形エポキシ樹脂	45	固形エポキシ樹脂	28
水酸値	合成ヘタライト	10	合成ヘタライト	10	モノエポキシ樹脂	10	合成ヘタライト	11	合成ヘタライト	11	合成ヘタライト	10	合成ヘタライト	11
機溶剤	ジメチルホルムアミド	400	メチルエチルケトン	400	テトラヒドロフラン	400	ジメチルホルムアミド	430	メチルエチルケトン	430	ジメチルホルムアミド	500	ジメチルホルムアミド	480
その他	ジシアンジアミド	3.15	ジシアンジアミド	3.15	ジシアンジアミド	3.15	—	—	—	—	ジシアンジアミド	3.15	—	—
	変性イミダゾール	1.35	変性イミダゾール	1.35	変性イミダゾール	1.35	—	—	—	—	変性イミダゾール	1.35	水酸化マグネシウム	45
層間距離 (nm)	3.5<		3.5<		3.5<		3.5<		3.5<		3.5<		3.5<	
下の積層体から露出している層の割合 (%)	10<		10<		10<		10<		10<		10<		10<	
露出形状	○		○		○		○		○		○		○	
露出面積 (W/m ²)	420		440		425		310		330		240		200	
露出部の強度 (kPa)	8		7		7		8		7		9		9	

樹脂層	層状硅酸 有機溶	その他	平均層間 (nm)	5層以下の として分散し 固状硅酸塩の	燃焼時 保持率	最大熱流 (kW/m ²)	燃焼残り 被膜強度
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[0128]The average interlaminar distance of the sheet silicate which each charge of insulating-substrate material produced in Examples 1, 2, 3, 4, 5, 6, and 7 from Table 1 contains is not less than 3 nm.

And the percentage of the sheet silicate currently distributed as a layered product of five or less layers is not less than 10%, and it excelled in the shape retentivity at the time of combustion. Since it was easy to form the sintered compact used as a fire-resistant tunic, the maximum heat release rate was slow and the yield stress (tunic intensity) of combustion residue was also 4.9 or more kPa. On the other hand, calcium carbonate did not distribute in layers, but the charge of insulating-substrate material of the comparative example 1 which used and produced calcium carbonate instead of the sheet silicate had the bad shape retentivity at the time of combustion, its maximum heat release rate was quite quick, and its yield stress (tunic intensity) of combustion residue was extremely low.

[0129]

[Effect of the Invention]According to this invention, it excels in dynamic physical properties, dimensional stability, heat resistance, etc., and the charge of insulating-substrate material which has the outstanding fire retardancy especially by the shape retention effect at the time of combustion, a laminate sheet, a printed circuit board, copper foil with resin, copper clad laminate, a polyimide film, the film for TAB, and prepreg can be provided.

[Translation done.]